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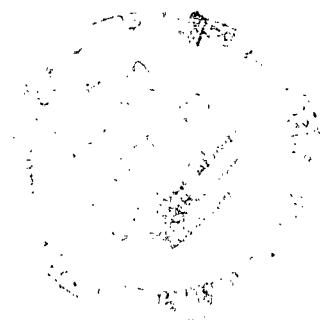


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MASS SPECTROMETRIC INVESTIGATION
OF VAPORIZATION THERMODYNAMICS
OF YTTRIUM DICARBIDE - CARBON SYSTEM
AND DISSOCIATION ENERGY OF YTTRIUM
DICARBIDE AND TETRACARBIDE

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16. Abstract <p>The Knudsen effusion method was used in conjunction with a double focusing mass spectrometer to study the vaporization of the yttrium dicarbide-carbon system. Over the temperature range from 2270 to 2550 K the vapor pressures for yttrium, yttrium dicarbide, and yttrium tetracarbide were measured. Experimentally determined enthalpies were combined with published thermodynamic data to yield the atomization energies of yttrium dicarbide and yttrium tetracarbide molecules:</p> $\text{YC}_2 = \text{Y} + 2\text{C} \quad D_{0,\text{atom}}^0 = 1229 \pm 17 \text{ kJ mole}^{-1} (294 \pm 4 \text{ kcal mole}^{-1})$ $\text{YC}_4 = \text{Y} + 4\text{C} \quad D_{0,\text{atom}}^0 = 2461 \pm 18 \text{ kJ mole}^{-1} (588 \pm 4 \text{ kcal mole}^{-1})$ <p>The heat of formation of solid yttrium dicarbide was calculated as</p> $\Delta H_{298,\text{f}}^0 = -91 \pm 17 \text{ kJ mole}^{-1} (-22 \pm 4 \text{ kcal mole}^{-1}).$					
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SUMMARY

The Knudsen effusion method was used in conjunction with a double focusing mass spectrometer to study the vaporization of the yttrium dicarbide-carbon system. Over the temperature range from 2270 to 2550 K the measured vapor pressures for yttrium, yttrium dicarbide, and yttrium tetracarbide were found to be

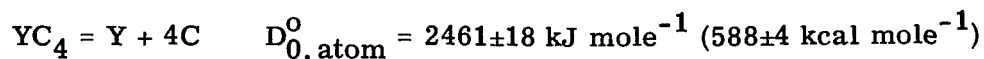
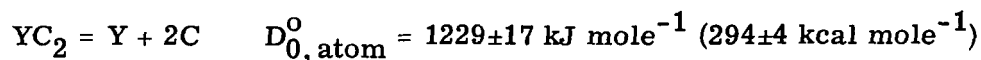
$$\log P_Y = -2.423 \cdot 10^4/T + 9.45$$

$$\log P_{YC_2} = -3.286 \cdot 10^4/T + 11.95$$

$$\log P_{YC_4} = -4.456 \cdot 10^4/T + 14.72$$

where the units of pressure are newtons per square meter.

Experimentally determined enthalpies were combined with published thermodynamic data to yield the atomization energies of the yttrium dicarbide and yttrium tetracarbide molecules



The heat of formation of solid yttrium dicarbide was calculated as

$$\Delta H_{298, f}^0 = -91 \pm 17 \text{ kJ mole}^{-1} \quad (-22 \pm 4 \text{ kcal mole}^{-1})$$

INTRODUCTION

Recently De Maria et al. (ref. 1) made a high temperature, molecular-beam mass spectrometric investigation of the vapor phase in thermodynamic equilibrium with the yttrium-carbon condensed system. Over the temperature range from 2075 to 2340 K, yttrium (Y) and yttrium dicarbide (YC_2) were reported to be important species in the vapor phase. These investigators did not detect the yttrium tetracarbide (YC_4) molecule in the vapor phase. However, other studies of rare-earth-carbon systems have shown both the tetracarbide and dicarbide species to exist as rather stable molecules. For cerium, neodymium, promethium, and holmium both the dicarbide and tetracarbide vapor phase molecular species have been reported (refs. 2 to 4). The purpose of our investigation was (1) to determine whether the YC_4 molecule could be detected by extending the temperature range (ref. 1) used in the previous investigation, and (2) to evaluate the thermodynamic properties of $\text{YC}_2(\text{g})$, $\text{YC}_4(\text{g})$, and $\text{YC}_2(\text{s})$.

APPARATUS

The Knudsen cell double focusing mass spectrometer system used in this study is basically the same as described previously (ref. 5). The only significant modifications to the system involved the Knudsen cell (its construction, blackbody holes, and surrounding heat shields), the addition of a device for the direct recording of ionization efficiency curves, and the installation of an ion counting system at the anode of the electron multiplier ion detector.

Knudsen Cell

The tungsten Knudsen cell was cylindrical with 0.48 centimeter walls and an inside diameter of 0.97 centimeter by 1.60 centimeter high. A tight fitting doubly stepped lid, 0.48 centimeter thick, was used to close the cell. A zero length 0.076 centimeter diameter effusion orifice was spark machined into the cylindrical side wall of the cell at a height of 1.27 centimeters from the bottom outside. Three blackbody holes were spark machined into the cell at heights of 0.64, 1.27, and 1.91 centimeters from the outside bottom and 180° opposite the effusion orifice. The blackbody holes were nominally 0.051 centimeter in diameter and 0.457 centimeter deep.

For all experiments reported here the Knudsen cell was fitted with a graphite liner made from Ultra Carbon UFS graphite. The liner had a 0.10-centimeter wall thickness and a lid with a single step. A 0.25-centimeter diameter hole in the wall of the liner was arranged to line up concentrically with the effusion orifice.

The heat shields were the same as those described previously (ref. 5) except in two respects. The newer shields had separate removable lids and were made of 0.025-centimeter tantalum rather than the 0.013-centimeter tantalum used before. The thicker tantalum was found to be less subject to warpage and made a generally more rigid assembly without significantly degrading the heating characteristics of the heat shield assembly.

Ionization Efficiency Curve Recording Equipment

A variable speed motor driven 10-turn linear potentiometer was used to vary the ionizing voltage when recording ionization efficiency curves. The ionizing voltage was applied to both the ion source and the X channel of an X-Y recorder. The Y channel of the X-Y recorder was driven by the electrometer connected to the output of the ion detecting electron multiplier. A special isolating device (described in patent application no. 632153 by Krawczonek and Finke) was used to isolate the accelerator high voltage from the X-Y recorder. The isolator amplifies the ionizing voltage, voltage-to-frequency converts it and uses this signal to drive a lamp. The lamp output, in turn, is detected with a photodetector, frequency-to-voltage converted and used to drive the X channel of the recorder. High voltage isolation is provided by proper separation of the lamp and photodiode detector and for the system used isolation was provided to 25 kilovolts.

Ion Counting System

The output of the electron multiplier was brought to a shielded switch which allowed the electron multiplier anode to be connected to either the electrometer or the ion counting unit. The usual procedure for counting was to locate and to sit on the peak maximum by using the electrometer and then to switch to the ion counting mode.

The ion counting system consisted of a Johnston Laboratories, Inc., PAD-1 pulse amplifier-discriminator and a high frequency digital counter.

Proper operation of the ion counting unit was established by vaporizing gold in the Knudsen cell and studying the mass spectrometer ion output alternately with the electrometer and ion counter. The electrometer output current I_e is related to the number of ions incident on the electron multiplier by the following equation:

$$N = \frac{I_e}{\gamma e^-} \quad (1)$$

where N is the number of ions per second striking the first dynode of the multiplier,

γ is the multiplier gain, and e^- is the charge of the electron. The multiplier gain was measured for gold by ion counting and using formula (1). Next, the multiplier gain was measured directly by a comparison of the outputs when the electrometer was connected to the multiplier anode and when the electrometer was connected to a Faraday collector preceding the multiplier. The direct gain measurement for gold at maximum multiplier voltage yielded a value of 1.15×10^7 while ion counting gave a value of 1.00×10^7 .

The ion counter was further checked by plotting various mass to charge (m/e) ratio peaks as determined by ion counting and superimposing them on the corresponding peaks directly recorded with the electrometer. Agreement in all cases was found to be excellent. Checks of the ion counter were made only to a maximum count rate of 160 kilocounts per second and the unit was deemed to operate satisfactorily to this rate. The ion counting system was used primarily to obtain the multiplier gains for various ions.

PROCEDURE AND EXPERIMENTAL RESULTS

Sample

The graphite Knudsen cell liner was loaded with a homogeneous mixture of 0.023 gram of Ultra Carbon Grade UFS-4 powdered graphite (C) and 0.062 gram of yttrium (Y) metal filings to give an approximate atomic ratio of C to Y of 2.7 to 1.0. The yttrium metal filings were obtained from an ingot of 99.9 percent purity supplied by Research Chemicals of Phoenix, Arizona. Spectrographic analysis indicated that aluminum, silicon, magnesium, and iron were trace impurities in the graphite powder and that silicon, magnesium, vanadium, chromium, iron, copper, and zirconium were the major metallic impurities in the yttrium.

The yttrium dicarbide (YC_2) sample was prepared in situ in the Knudsen cell chamber of the mass spectrometer. The temperature of the Knudsen cell was raised over a period of several hours to a temperature of 1820 K. This temperature is above the melting point of yttrium. The cell was held at this temperature overnight and the background pressure in the Knudsen cell vacuum chamber was in the low 10^{-6} torr range.

After the experiment the sample residue was removed from the Knudsen cell for visual inspection and X-ray diffraction analysis. Immediately upon removal the residue was found to be a loosely sintered cylinder with a black to dark gray metallic color. When broken into pieces this residue showed small amounts of gold-colored solid. The yttrium dicarbide is reported to be gold-colored (ref. 6). Powder X-ray diffraction samples of the residue were prepared quickly after the residue was removed from the Knudsen cell. The samples were attached to a quartz fiber and protected from the ambient atmosphere by coating with Apiezon grease. The X-ray powder pattern obtained

for such samples showed that the sample was a mixture of YC_2 and graphite. The experimental d (lattice spacing) values for YC_2 agreed within 0.2 percent with those reported in reference 7.

The portion of the residue that was not protected from the ambient atmosphere was found to degrade very rapidly, apparently by oxidation and/or hydrolysis (ref. 8). Microscopic observation of the unprotected residue showed the crystal faces changing from their bright metallic appearance to a dull gray powder within a matter of only a few minutes. After extended atmospheric exposure the residue changed completely to an ash-like powder. A strong calcium carbide odor was detected above the degraded residue, and this has been taken as an indication of hydrolysis. X-ray analysis of the degraded residue indicated that it was a mixture of graphite and a second phase which gave a number of very weak lines. Because of the low intensity of these lines it was concluded that the major portion of the degraded residue was amorphous.

Vapor Species Identification and Measurements

After initial sample preparation the Knudsen cell temperature was raised to 2380 K and ion peak identification was initiated. The Y^+ , YC_2^+ , and YC_4^+ peaks were readily identified by their ratios of mass to charge and isotopic abundance distributions. Proof as to which species were originating from the Knudsen cell was established by shutter profile measurements. The measured ion currents for each species originating from the Knudsen cell correspond to the difference between the output signal measured with the shutter in the open and closed positions, respectively. The shutter effect for all yttrium containing ions was essentially 100 percent.

All ion intensity measurements were made with ionizing electrons of 20 electron volts (eV) energy and an anode current of 150 microamperes. For all experiments reported here the resolution of the mass spectrometer was 1800 based on the 10 percent valley definition. This resolution was sufficient to separate the organic background peaks from the metal ion peaks at the same nominal mass to charge ratio. An example of a typical portion of the mass spectrum is shown in figure 1.

At a temperature of 2500 K additional peaks corresponding to the ions of carbon, yttrium carbide, yttrium oxide, yttrium fluoride (C^+ , C_2^+ , C_3^+ , YC^+ , YO^+ , YF_2^+), and traces of metallic ions titanium, iron, cobalt, nickel, zirconium, and molybdenum (Ti^+ , Fe^+ , Co^+ , Ni^+ , Zr^+ , and Mo^+) were observed. All of these species exhibited a 100 percent shutter effect.

The observation of YF^+ and YF_2^+ was not unexpected since the fluoride is known to be a common impurity in yttrium metal which is produced by reduction of the fluoride with calcium metal in a calcium fluoride lined bomb (ref. 9). Studies of yttrium fluoride have shown YF , YF_2 , and YF_3 to be major molecular species (ref. 10).

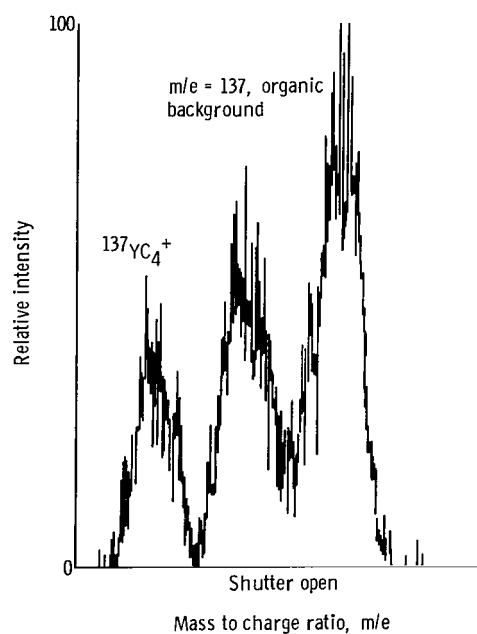
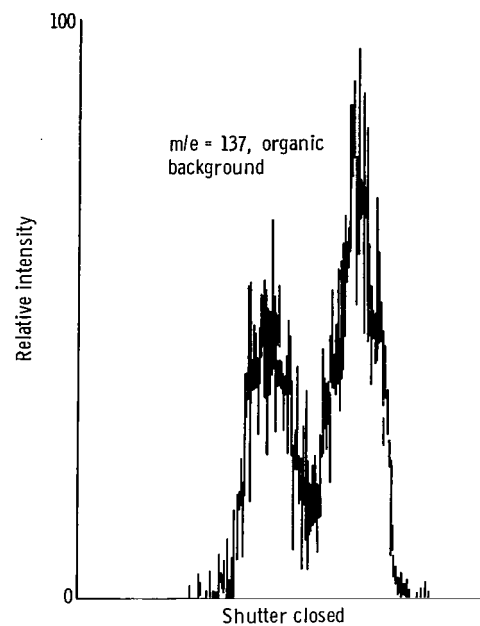


Figure 1. - Typical spectrum in region of mass to charge ratio of 137 showing the resolution of YC_4^+ and organic background ions and shutter effect.

The low intensity peak observed at $m/e = 105$ is assigned to the YO^+ ion. This ion derives from YO which either effuses from the Knudsen cell or is formed on its exterior or the heat shields.

At the highest temperature (2552 K) of this study a careful search was made for additional ion species of higher molecular weight containing Y and C. No such species were detected and it must therefore be presumed that if any were present their partial pressure was below 5×10^{-5} newtons per square meter which is the lower detection limit of our system.

The pressure calibration of the Knudsen cell - mass spectrometer system was obtained by the integral gold calibration technique (ref. 11). Several milligrams of gold were quantitatively vaporized at temperatures between 1550 and 2150 K. Intensity was continuously recorded and the intensity-time curves were subsequently integrated.

Ion intensities of Y^+ , YC_2^+ , and YC_4^+ were measured at various temperatures in the range from 2274 to 2552 K. Data points were taken for both increasing and decreasing sequences of temperature. Ion intensities at any particular temperature were found to remain constant for a period of at least 20 hours.

Appearance Potentials

Ionization efficiency curves were recorded for Y^+ , YC_2^+ , and YC_4^+ ; these are presented in figures 2 to 4. Appearance potentials were measured for Y^+ , YC^+ , YC_2^+ , and YC_4^+ by recording the initial portion of the ionization efficiency curves on an expanded scale and applying the linear extrapolation method. Some typical expanded scale curves are presented in figure 5. The known ionization potential of 6.38 eV for Y (ref. 12) was used as an internal standard for calibration of the electron energy scale.

The relative intensities at 2552 K and appearance potentials for C_3^+ and the yttrium containing ions are listed in table I. The value of 6.7 ± 0.3 eV for the appearance potential of YC_2^+ is in good agreement with the value 6.8 ± 0.3 eV reported by De Maria et al. (ref. 1). The value of 7.0 ± 0.3 eV for YC_4^+ is in accord with the vague trend observed for CeC_4^+ (ref. 2) and NdC_4^+ (ref. 3) in that the appearance potential for the tetracarbide is higher than that of the metal and metal dicarbide. The low values observed for the appearance potentials thus establish that the Y^+ , YC_2^+ , and YC_4^+ ions are parent ions formed directly by electron impact of Y, YC_2 , and YC_4 molecules.

In the case of YC^+ the appearance potential was determined to be 14 ± 1 eV with an intensity ratio of YC_2^+/YC^+ of about 100/1. This value for the appearance potential indicates that the YC^+ ion is a fragment from the YC_2 parent. Our value agrees satisfactorily with that reported by De Maria et al. (ref. 1), namely, 13.4 ± 0.5 eV with an intensity ratio also of approximately 100/1.

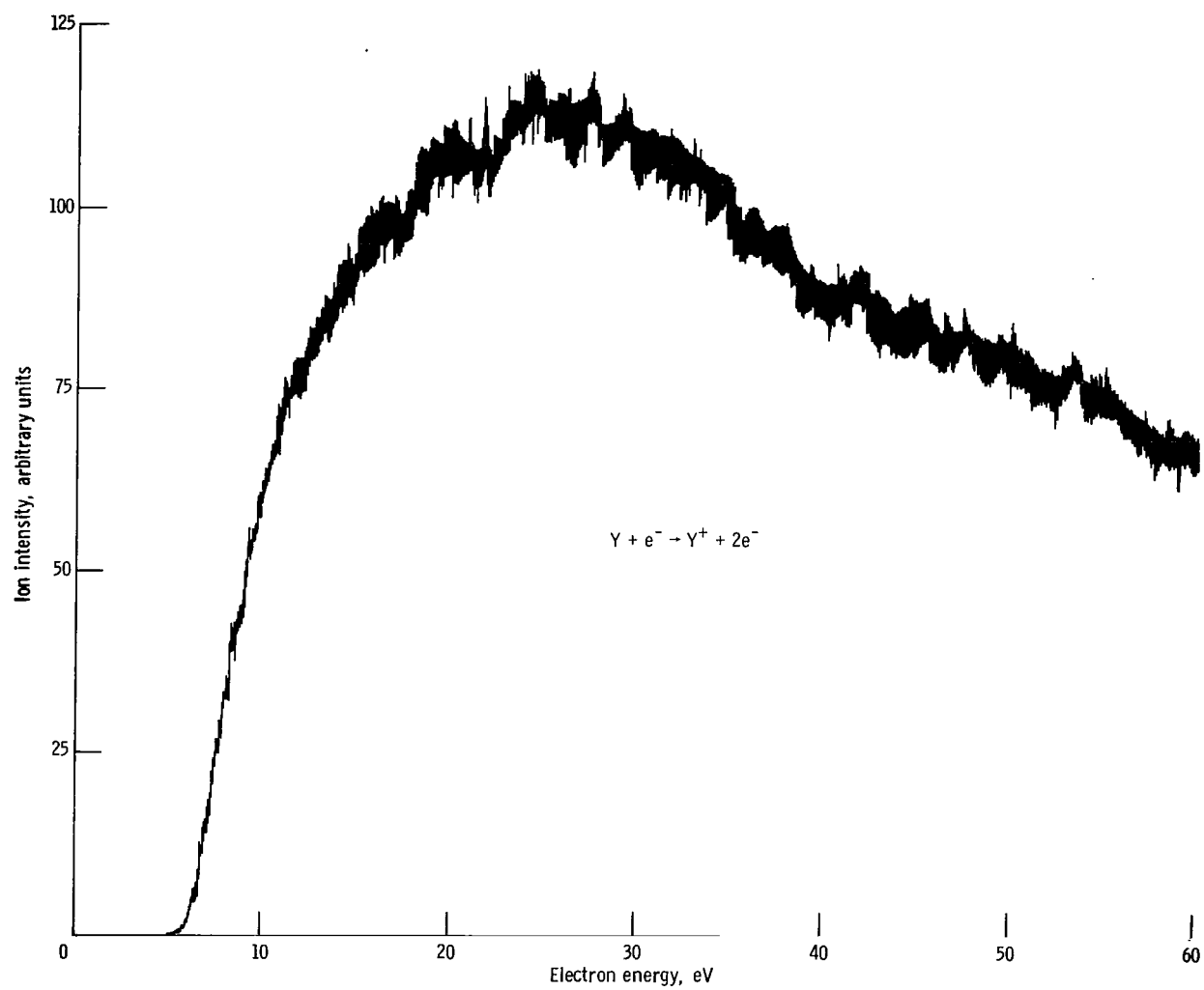


Figure 2. - Ionization efficiency curve for Y^+ .

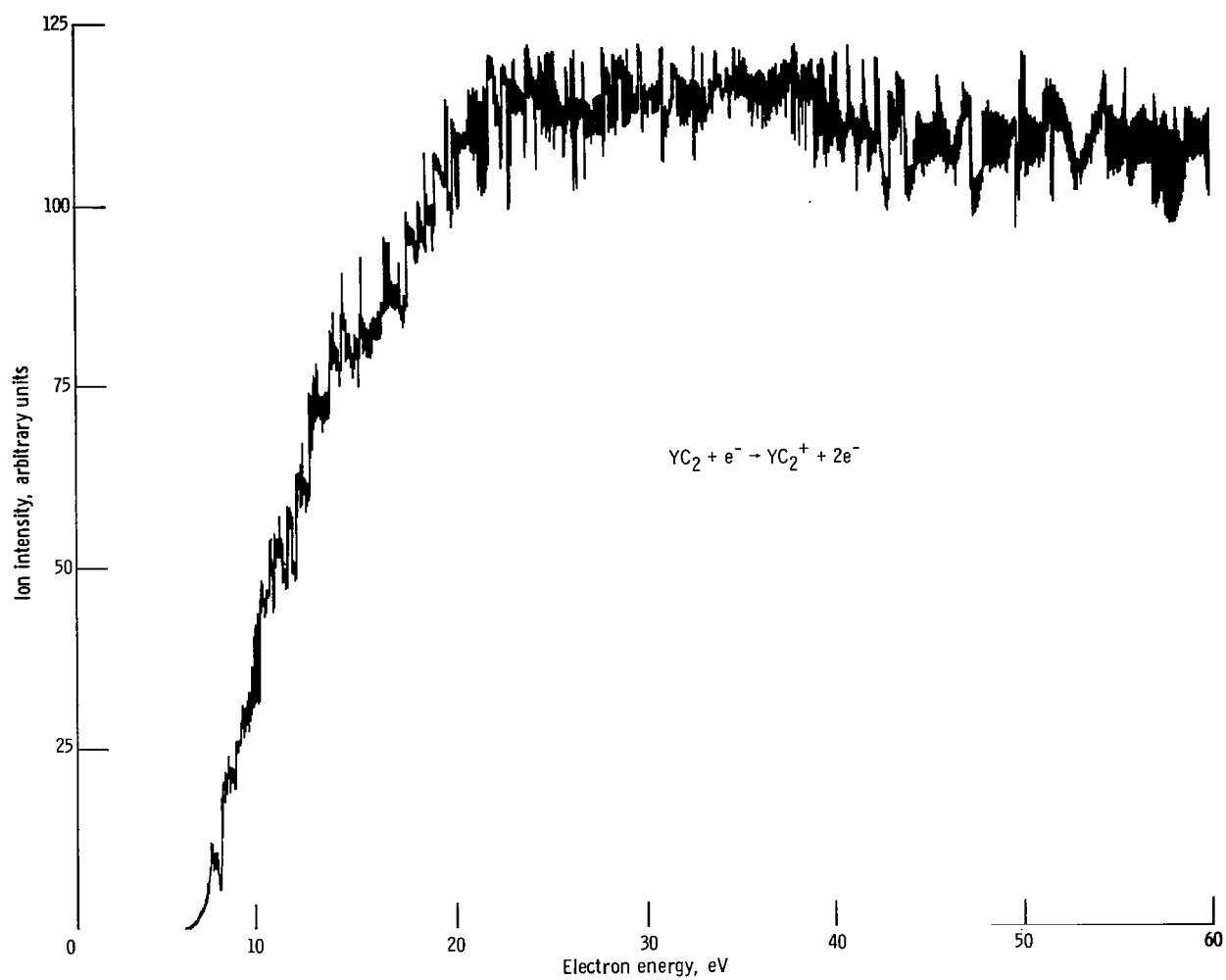


Figure 3. - Ionization efficiency curve for YC_2^+ .

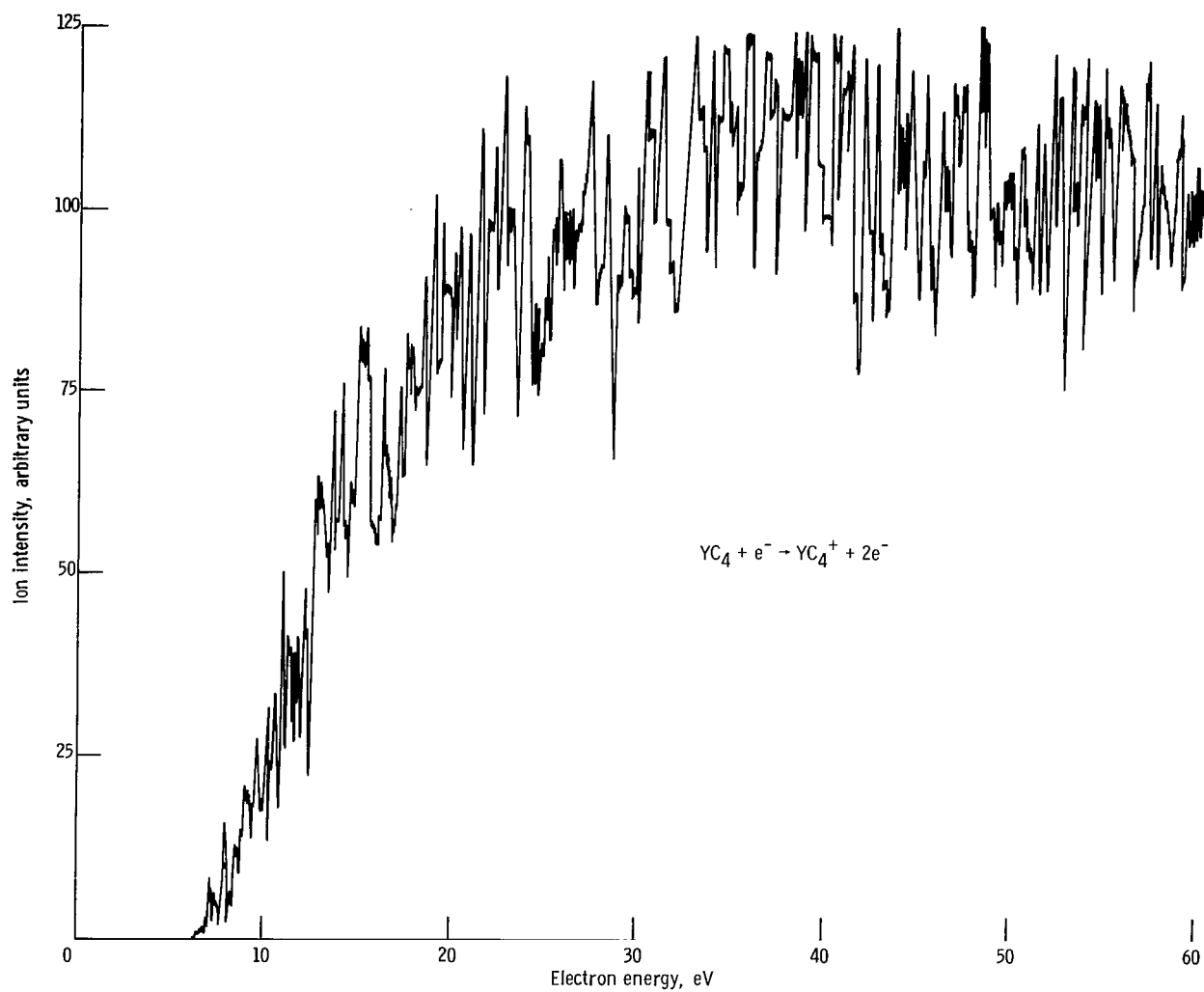


Figure 4. - Ionization efficiency curve for YC_4^+ .

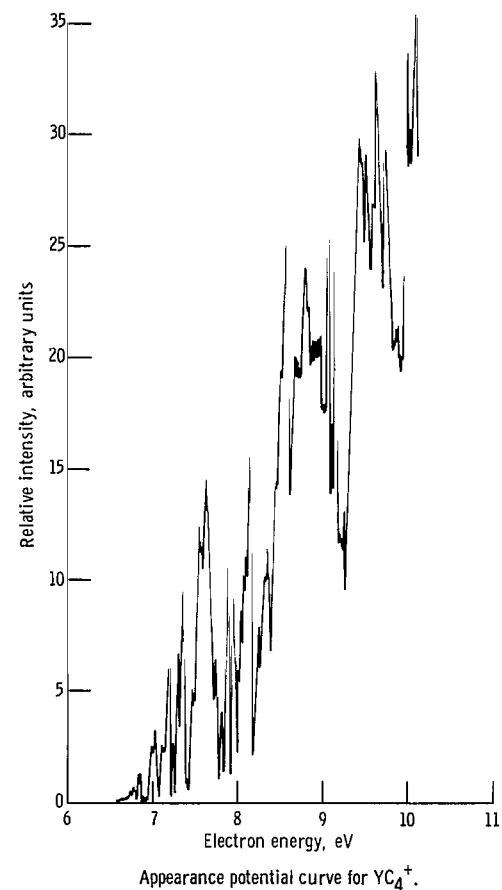
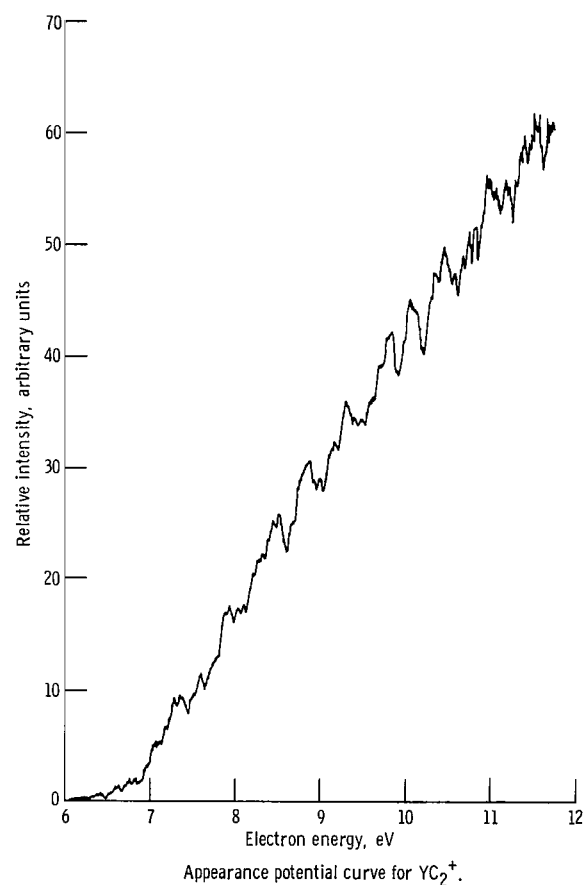
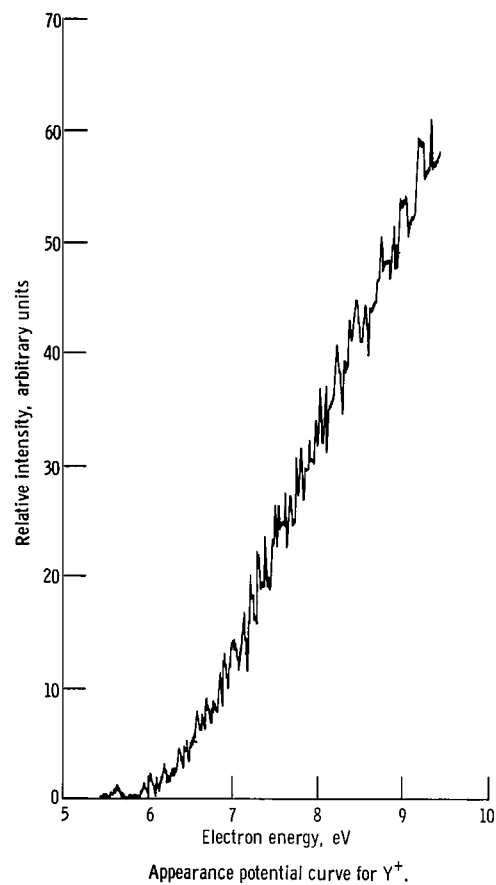


Figure 5. - Appearance potential curves for Y^+ , YC_2^+ , and YC_4^+ .

TABLE I. - RELATIVE ION INTENSITIES AT 2552 K (20 eV
ELECTRONS) AND APPEARANCE POTENTIALS FOR
CARBON AND YTTRIUM CONTAINING SPECIES

Ion	Parent	Relative intensity	Appearance potential, eV	
			This report	Literature
$^{36}\text{C}_3^+$	C_3	0.20	12.1 ± 0.3	^a 12.6
$^{89}\text{Y}^+$	Y	1.00	^a 6.38 (standard)	-----
$^{101}\text{YC}^+$	YC_2	1.9×10^{-3}	14 ± 1	^b 13.4 \pm 0.5
$^{105}\text{YO}^+$	YO	4.1×10^{-4}	-----	-----
$^{108}\text{YF}^+$	YF, YF_2	8.7×10^{-2}	-----	-----
$^{113}\text{YC}_2^+$	YC_2	0.20	6.7 ± 0.3	^b 6.8 \pm 0.3
$^{127}\text{YF}_2^+$	YF_3, YF_2	3.4×10^{-3}	-----	-----
$^{137}\text{YC}_4^+$	YC_4	4.0×10^{-3}	7.0 ± 0.3	-----

^aRef. 12.

^bRef. 1.

The appearance potential of 12.1 ± 0.3 eV for C_3^+ is in reasonable agreement with that previously reported for the parent C_3^+ ion (ref. 12).

CALCULATIONS

Pressures

Measured ion currents, I_i , for Y^+ , YC_2^+ , and YC_4^+ were converted to the corresponding partial pressures P_i at temperature T by the relation

$$P_i = \frac{k I_i T E_i}{\sigma_i \gamma_i n_i} \quad (2)$$

where k is the calibration constant determined by the gold calibration, σ_i is the relative maximum ionization cross section, E_i is the experimentally determined factor to correct ion intensities measured at 20 eV to the maximum of the ionization efficiency curve (ratio of intensity at maximum to intensity at measurement electron energy), γ_i

TABLE II. - MULTIPLIER GAIN, CROSS SECTION, AND
ION INTENSITY CORRECTION FACTOR FOR
VARIOUS IONS

Ion	Multiplier gain, γ_i	Cross section, σ_i	Intensity correction factor, E_i
Y^+	1.13×10^7	8.64	1.10
YC_2^+	1.37	12.10	1.09
YC_4^+	1.64	15.56	1.24
Au^+	8.27×10^6	6.46	1.42

TABLE III. - PARTIAL PRESSURES OF GASEOUS SPECIES OVER THE YTTRIUM
DICARBIDE-GRAPHITE SYSTEM, $(YC_2)(s)-C(s)$

Temper- ature, K	Partial pressure, N/m^2			Temper- ature, K	Partial pressure, N/m^2		
	P_Y	P_{YC_2}	P_{YC_4}		P_Y	P_{YC_2}	P_{YC_4}
2379	1.67×10^{-1}	1.26×10^{-2}	1.07×10^{-4}	2412	2.71×10^{-1}	2.02×10^{-2}	1.69×10^{-4}
2419	2.61	2.33	2.21	2274	6.17×10^{-2}	3.26×10^{-3}	-----
2461	3.89	3.65	3.47	2330	1.12×10^{-1}	7.22	-----
2504	5.83	6.91	7.63	2368	1.60	1.18×10^{-2}	-----
2529	7.47	8.94	1.09×10^{-3}	2473	3.75	4.14	-----
2493	6.53	7.35	8.18×10^{-4}	2498	5.37	6.51	9.61×10^{-4}
2478	5.33	5.08	5.57	2552	7.72	1.10×10^{-1}	2.01×10^{-3}
2457	4.30	3.53	2.91				

is the relative multiplier gain, and n_i is the fractional isotopic abundance of the species i . Table II lists σ_i , γ_i , and E_i for Y^+ , YC_2^+ , YC_4^+ , and Au^+ . The relative maximum ionization cross sections for atoms were taken from Mann (ref. 13). The cross sections for YC_2 and YC_4 were obtained by summing the cross sections for Y and two or four carbon atoms, respectively.

Calculated partial pressures for Y, YC_2 , and YC_4 are listed in table III. Vapor pressures for Y, YC_2 , and YC_4 are plotted against reciprocal temperature in figure 6.

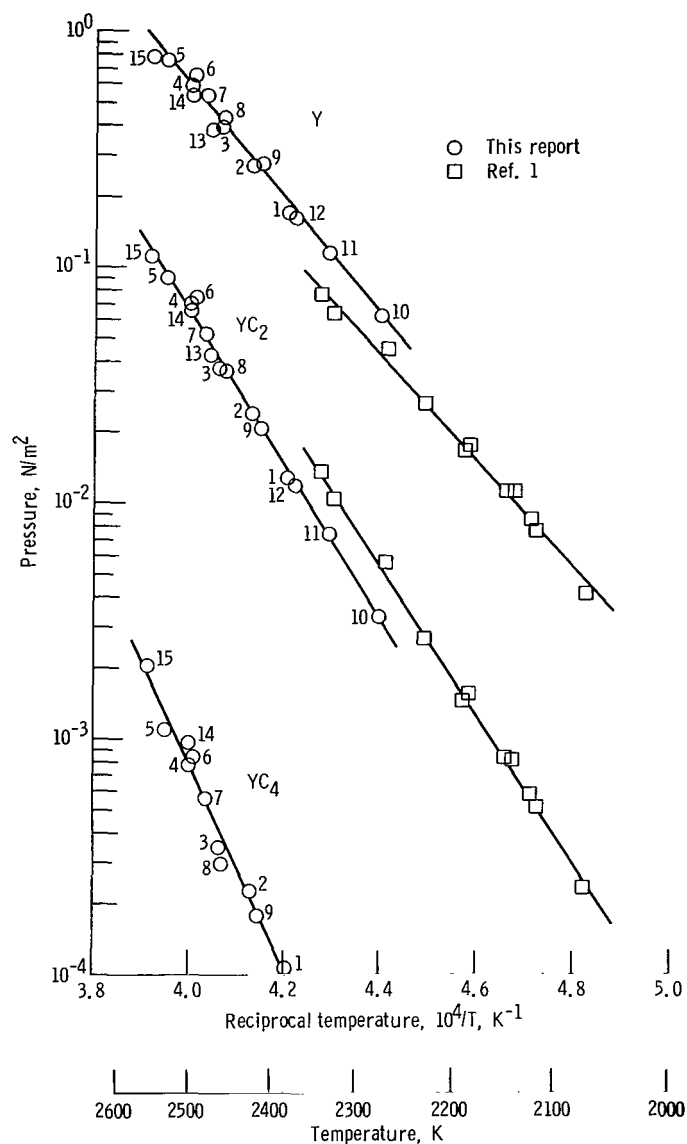


Figure 6. - Equilibrium pressures of Y, YC₂, and YC₄ over YC₂ - C(s) as function of reciprocal temperature. Points are numbered chronologically.

The values of the pressures were computer fit by the least squares method to equations of the form

$$\log P \text{ (N/m}^2\text{)} = -\frac{A}{T} + B \quad (3)$$

Values of the parameters **A** and **B** are listed in table IV.

TABLE IV. - LEAST-SQUARES PARAMETERS OF EQUATIONS

$$\log P \text{ (N/m}^2\text{)} = -A/T + B \text{ FOR Y, YC}_2, \text{ AND YC}_4$$

Species	Least squares parameters ^a		Temperature range, K	Mean tem- perature, K
	A	B		
Y	24230±850	9.45±0.35	2270 - 2550	2439
YC ₂	32860±690	11.95±0.28	2270 - 2550	2439
YC ₄	44560±2380	14.72±0.96	2380 - 2550	2470

^aThe errors are standard deviations of the slope and intercept and do not represent the overall estimated error. See text.

Heats of Reactions

A number of equilibrium reactions may be considered in a thermodynamic analysis of the vaporization for the Y-C system. Seven such reactions are listed in table V as reactions (1) to (7). Reactions (1) to (4) are termed pressure independent since the equilibrium constant depends only on the ratio of corrected intensities and not on the pressure relating calibration constant. In figure 7 the appropriate corrected ion intensity ratios are plotted against the reciprocal temperature for the pressure independent reactions (1) to (3). The second-law heats, ΔH_T^0 , for these reactions were obtained from the least squares slopes of the lines in figure 7. The second-law heats for the pressure dependent reactions ((5) to (7)) were obtained from the least squares slopes of the $\log P_i$ versus $1/T$ plots presented in figure 6 for Y(g), YC₂(g), and YC₄(g), respectively. The uncertainties listed for ΔH_T^0 in table V are those arising from the standard deviations of the data points in figures 6 and 7. The ΔH_{298}^0 or ΔH_0^0 values were obtained through the use of the $H_T^0 - H_{298}^0$ or $H_T^0 - H_0^0$ values for the various constituents. The overall estimated errors for the second law heats (for ΔH_{298}^0 and ΔH_0^0) were obtained by combining the standard deviations of the data points with the uncertainty due to an estimated maximum temperature error of ±10 K.

Our assumption of unit activity for C(s) and YC₂(s) is very reasonable considering

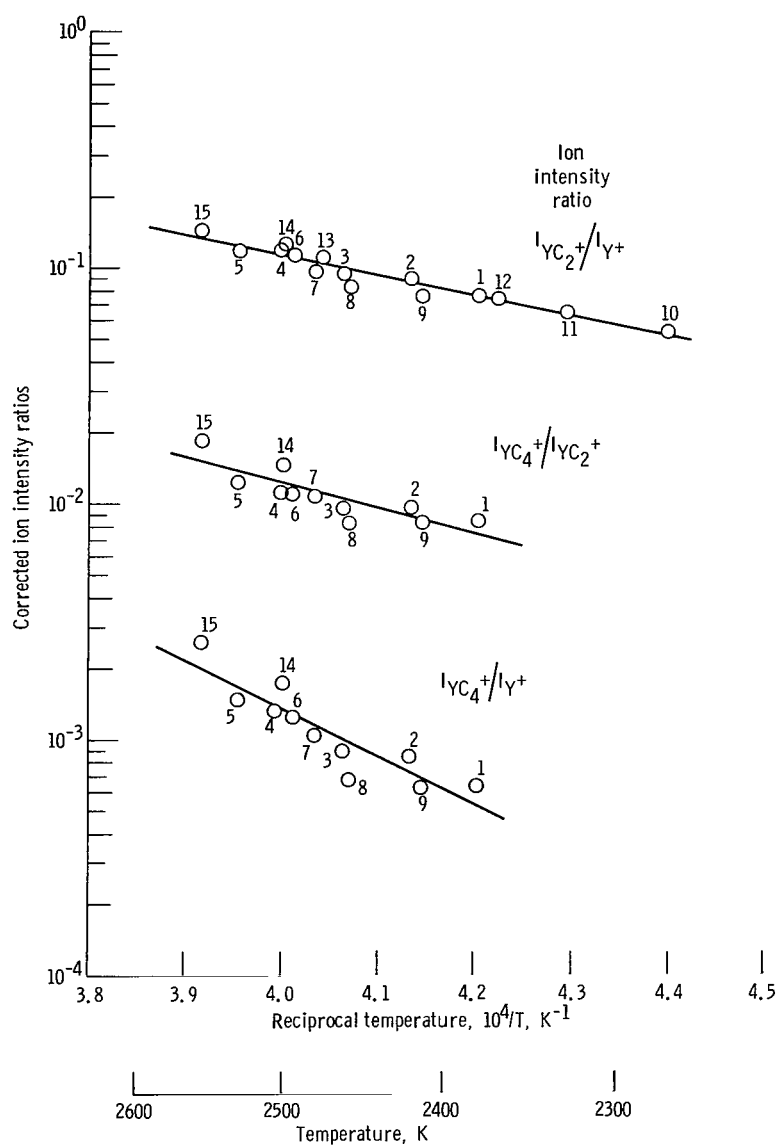


Figure 7. - Ion intensity ratios as function of reciprocal temperature. Points are numbered chronologically.

TABLE V. - ENTHALPIES FOR REACTION IN YTTRIUM-CARBON SYSTEM

Reaction	Second law			Third law	
	Enthalpy, kJ mole ⁻¹				
	ΔH_T^O (a)	ΔH_0^O (b)	ΔH_{298}^O (b)	ΔH_0^O (b)	ΔH_{298}^O (b)
(1) Y(g) + 2C(s) = YC ₂ (g)	^c 165.3±12.1	179.9±14.6 ^d 175.7±16.7	-----	190.3±17.2 ^d 171.5±12.6	-----
(2) YC ₂ (g) + 2C(s) = YC ₄ (g)	^e 199.6±40.6	192.5±43.9	-----	186.6±17.2	-----
(3) Y(g) + 4C(s) = YC ₄ (g)	^e 392.9±59.4	400.8±67.8	-----	377.3±17.6	-----
(4) Y(g) + YC ₄ (g) = 2YC ₂ (g)	^e -6.3±28.0	15.9±28.0	-----	4.16±17.6	-----
(5) YC ₂ (s) = Y(g) + 2C(s)	^c 464.0±16.3	-----	519.2±28.5	-----	516.1±17.6 ^d 523.0±16.7
(6) YC ₂ (s) = YC ₂ (g)	^c 629.3±13.0	-----	700.4±34.7	-----	707.9±17.6
(7) YC ₂ (s) + 2C(s) = YC ₄ (g)	^e 853.1±45.6	-----	921.7±84.1	-----	898.2±18.0

^aErrors are standard deviations of the slopes.^bErrors are overall estimated uncertainty. See text.^cTemperature, 2439 K.^dRef. 1.^eTemperature, 2470 K.

that both C and YC_2 were identified in the condensed phase in the sample residue after the experiment.

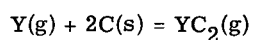
Third-law heats (ΔH_{298}^0 or ΔH_0^0) for reactions (1) to (7) were calculated according to the relations

$$\Delta H_{298}^0 = -2.303 RT \log K_p - T \Delta \left(\frac{G_T^0 - H_{298}^0}{T} \right) \quad (4)$$

$$\Delta H_0^0 = -2.303 RT \log K_p - T \Delta \left(\frac{G_T^0 - H_0^0}{T} \right) \quad (5)$$

where K_p is the equilibrium constant of the reaction with stoichiometric coefficient m_i , K_p is equal to $\prod P_i^{m_i}$, R is the gas constant and $\Delta \left[(G_T^0 - H_{298}^0)/T \right]$ and $\Delta \left[(G_T^0 - H_0^0)/T \right]$ are the change of the Gibbs' free energy function for the reaction. The values of the free energy functions used in the third-law heat calculations are discussed in a subsequent section. Calculated third-law heats for reactions (1), (3), and (5) are presented in tables VI to VIII together with other pertinent parameters for each data

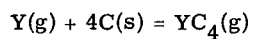
TABLE VI. - THIRD LAW ENTHALPIES FOR REACTION



Temperature, T, K	Logarithm of equilibrium constant, $\log K_p$	Change of free-energy function, $-\Delta \left[\left(G_T^0 - H_0^0 \right) / T \right],$ $\text{J deg}^{-1} \text{ mole}^{-1}$	Enthalpy, $\Delta H_0^0,$ kJ mole^{-1}
2379	-1.122	58.31	189.8
2419	-1.049	58.21	189.4
2461	-1.028	58.11	191.4
2504	-.9262	58.00	189.6
2529	-.9220	57.94	191.2
2493	-.9486	58.03	189.9
2478	-1.021	58.07	192.3
2457	-1.086	58.12	193.9
2412	-1.128	58.23	192.5
2274	-1.277	58.58	188.8
2330	-1.191	58.44	189.3
2368	-1.132	58.34	189.5
2473	-.9570	58.08	188.9
2498	-.9164	58.02	188.8
2552	-.8462	57.88	189.1
Average			^a 190.3±1.6

^a45.5±0.4 kcal mole⁻¹.

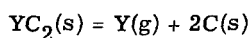
TABLE VII. - THIRD LAW ENTHALPIES FOR REACTION



Temperature, T, K	Logarithm of equilibrium constant, $\log K_p$	Change of free-energy $-\Delta[(G_T^0 - H_0^0)/T]$, J deg ⁻¹ mole ⁻¹	Enthalpy, ΔH_0^0 , kJ mole ⁻¹
2379	-3.193	96.08	374.0
2419	-3.072	96.03	374.6
2461	-3.050	95.98	379.9
2504	-2.883	95.92	378.4
2529	-2.836	95.89	379.8
2493	-2.902	95.94	377.7
2478	-2.981	95.96	379.2
2457	-3.170	95.98	384.9
2412	-3.205	96.04	379.6
2498	-2.747	95.93	371.0
2552	-2.584	95.86	370.9
Average			^a 377.3 ± 4.2

^a90.2 ± 1.0 kcal mole⁻¹.

TABLE VIII. - THIRD LAW ENTHALPIES FOR REACTION



Temperature, T, K	Logarithm of equilibrium constant, $\log K_p$	Change of free-energy function, $-\Delta[(G_T^0 - H_{298}^0)/T],$ $\text{J deg}^{-1} \text{ mole}^{-1}$	Enthalpy, $\Delta H_{298}^0,$ kJ mole^{-1}
2379	-5.783	106.99	517.9
2419	-5.588	106.63	516.7
2461	-5.416	106.26	516.7
2504	-5.240	105.89	516.3
2529	-5.133	105.69	515.8
2493	-5.191	105.98	512.0
2478	-5.279	106.11	513.4
2457	-5.373	106.30	513.9
2412	-5.574	106.69	514.7
2274	-6.215	107.99	516.1
2330	-5.955	107.44	516.0
2368	-5.801	107.09	516.6
2473	-5.432	106.16	519.7
2498	-5.276	105.94	517.0
2552	-5.118	105.51	519.3
Average			^a 516.1±2.1

^a123.4±0.5 kcal mole⁻¹.

point. Summarized third-law heats for all the various reactions are also included in table V. The estimated errors associated with ΔH_{298}^0 and ΔH_0^0 in table V were obtained by combining the standard deviations from the mean of all respective data points with estimated uncertainties in the values of K_p (± 50 percent), T (± 10 K), and $\Delta[(G_T^0 - H_{298}^0)/T]$ or $\Delta[(G_T^0 - H_0^0)/T][\pm 6.3 \text{ J deg}^{-1} \text{ mole}^{-1} (\pm 1.5 \text{ cal deg}^{-1} \text{ mole}^{-1})]$.

Thermodynamic Functions

The values of the heat content and free energy functions used for $\text{Y}(\text{g})$ were taken from Hultgren et al. (ref. 14) and those used for $\text{C}(\text{s})$ were taken from the JANAF tables (ref. 15). The heat content and free energy functions for $\text{YC}_2(\text{g})$ were calculated on the basis of estimated molecular parameters for an assumed linear, asymmetric Y-C-C molecule with a ground state statistical weight of 2. The molecular parameters used

were the same as those estimated by De Maria et al. (ref. 1). The Y-C and C-C interatomic distances were taken to be 239 and 131 picometers, respectively. The fundamental vibrational frequencies were calculated according to the valence force formulation given by Herzberg (ref. 16). The carbon-carbon stretching force constant was taken as 9.25×10^2 newtons per meter, the same as for C_2 . A value of 5.74×10^2 newtons per meter was used for the Y-C force constant, the same as that for Y-O. Assuming a value of 0.67×10^{-18} newton-meter per radian for the bending constant k_δ , the bending force constant $k_\delta/l_1 l_2$ had a value of 0.21×10^2 newtons per meter. The calculated frequencies in reciprocal centimeters were $\omega_1 = 659$, $\omega_2 = 436$ (doubly degenerate) and $\omega_3 = 1761$. The moment of inertia was calculated to be 30.8×10^{-39} gram-square centimeter. The values of the free energy functions calculated for $YC_2(g)$ using these parameters are essentially identical to those reported by De Maria et al. (ref. 1).

For $YC_4(g)$ a linear symmetric C-C-Y-C-C structure was assumed with a ground state statistical weight of 2 and the bond lengths were the same as mentioned previously. The method of Engler and Kohlrausch (ref. 17) was used to estimate the fundamental vibration frequencies. The following force constants were used: $f_{12} = 9.25 \times 10^2$ newtons per meter, $f_{23} = 5.74 \times 10^2$ newtons per meter, $f_{13} = f_{22} = 1.30 \times 10^2$ newtons per meter, $d_2 = k_\delta/l_{12} l_{23} = 0.21 \times 10^2$ newtons per meter, and $d_3 = k_\delta/(l_{23})^2 = 0.12 \times 10^2$ newtons per meter. The vibrational frequencies, in reciprocal centimeters, calculated for $YC_4(g)$ using these parameters are $\omega_1 = 768$, $\omega_2 = 1840$, $\omega_3 = 839$, $\omega_4 = 1782$, $\omega_5 = 90$, $\omega_6 = 437$, and $\omega_7 = 385$ with ω_5 to ω_7 doubly degenerate. The moment of inertia for YC_4 is calculated to be 77.4×10^{-39} gram-square centimeter.

The free energy functions for $YC_2(s)$ were taken directly from the estimated values given in reference 1. Heat content values were obtained by integrating the heat capacity equation of De Maria et al. (ref. 1).

The thermodynamic functions for $YC_2(g)$ and $YC_4(g)$ were calculated by using the rigid rotator-harmonic oscillator approximation. Pertinent heat contents and free energy functions for $YC_2(g)$, $YC_4(g)$, and $YC_2(s)$ are listed in table IX.

Dissociation Energies

The third-law heat of reaction (1) (table V), 190.3 ± 17.2 kilojoules per mole (45.5 ± 4.1 kcal mole $^{-1}$), was combined with the heat of formation of $C_2(g)$, $\Delta H_{0,f}^0 = 824.2 \pm 8.4$ kilojoules per mole (197.0 ± 2 kcal mole $^{-1}$) (ref. 15), to give the dissociation energy D_0^0 (Y- C_2):

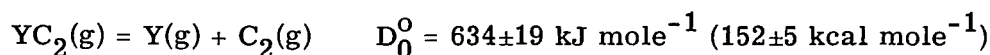


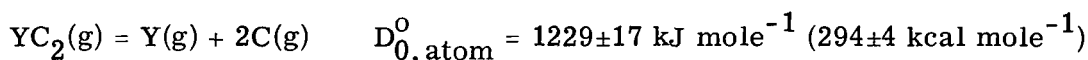
TABLE IX. - HEAT CONTENTS AND FREE-ENERGY FUNCTIONS FOR

YC₂(g), YC₄(g), AND YC₂(s)

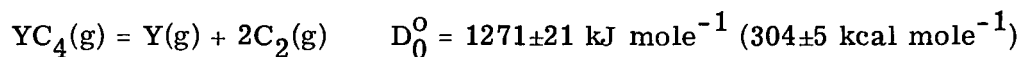
Temperature, T, K	YC ₂ (g)		YC ₄ (g)		YC ₂ (s) (a)	
	Heat content, H _T ^o - H ₀ ^o , kJ mole ⁻¹	Free-energy function, -(G _T ^o - H ₀ ^o)/T, J deg ⁻¹ mole ⁻¹	Heat content, H _T ^o - H ₀ ^o , kJ mole ⁻¹	Free-energy function, -(G _T ^o - H ₀ ^o)/T, J deg ⁻¹ mole ⁻¹	Heat content, H _T ^o - H ₂₉₈ ^o , kJ mole ⁻¹	Free-energy function, -(G _T ^o - H ₂₉₈ ^o)/T, J deg ⁻¹ mole ⁻¹
298	10.47	219.48	16.20	243.94	0	-----
1800	95.59	299.38	166.48	377.23	129.47	-----
1900	101.68	302.27	177.37	382.26	139.40	135.73
2000	107.77	305.02	188.30	387.06	149.48	139.54
2100	113.88	307.66	199.25	391.68	159.69	143.22
2200	120.00	310.19	210.22	396.11	170.03	146.77
2300	126.13	312.62	221.22	400.37	180.51	150.29
2400	132.27	314.96	232.23	404.47	191.12	153.64
2500	138.42	317.21	243.26	408.43	201.86	156.86
2600	144.57	319.39	254.30	412.26	212.74	159.95
2700	150.73	321.49	265.36	415.96	223.75	-----
2800	156.89	323.53	276.42	419.54	234.90	-----

^aRef. 1.

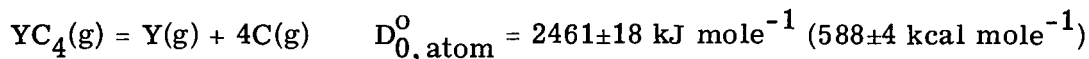
The atomization energy, D_{0,atom}^o, of YC₂ was obtained by combining the heat of reaction (1) with the heat of formation of C(g) which is 709.5±1.9 kilojoules per mole (169.6±0.5 kcal mole⁻¹) (ref. 15):



The heat of formation of C₂(g) was combined with the third-law heat of reaction (3), 377.3±17.6 kilojoules per mole (90.2±4.2 kcal mole⁻¹), to give the dissociation energy D₀^o(C₂-Y-C₂):



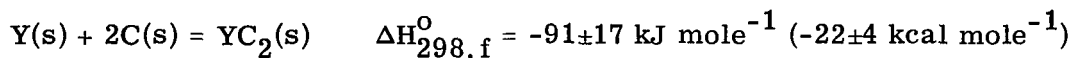
The atomization energy, D_{0,atom}^o, of YC₄(g) was calculated by combining the heat of reaction (3) with the heat of formation of C(g):



Identical values for $D_{0, \text{atom}}^{\circ}$ are obtained if the redundant reactions (2) or (4) are used as a starting point to derive this energy.

Heat of Formation of $\text{YC}_2(\text{s})$

The heat of formation of the condensed phase of YC_2 was obtained by combining the heat of reaction (5), 516.1 ± 17.6 kilojoules per mole (123.4 ± 0.5 kcal mole⁻¹), with the heat of vaporization, $\Delta H_{298, \text{vap}}^{\circ} = 427.7 \pm 2.1$ kilojoules per mole (101.5 ± 0.5 kcal mole⁻¹), (ref. 14) of yttrium:



DISCUSSION

The absence of any severe trend in the third-law heats as a function of temperature serves to indicate that no large systematic temperature error existed. Furthermore, the good agreement between second- and third-law values for all reactions demonstrates that no large systematic error was present and that the assumptions concerning the ionization cross sections and estimated thermodynamic functions were adequate. Particularly notable are the excellent agreements for reactions (5) and (6) which involve $\text{YC}_2(\text{s})$. This agreement provides support for the contention that $\text{YC}_2(\text{s})$ is the yttrium-carbon phase in equilibrium with the $\text{C}(\text{s})$ and the vapor phase.

The estimated overall uncertainties for the third-law heats are generally smaller than those associated with the corresponding second-law heats. Because the second-law heats are very sensitive to relatively small temperature errors, and considering the relatively small temperature interval covered by the measurements together with the number of experimental points obtained, the third-law values are recommended as the more accurate enthalpies.

The results obtained in the present investigation are generally in good agreement with those of De Maria et al. (ref. 1). The vapor pressures of Y and YC_2 over the $\text{YC}_2\text{-C}$ condensed phase compare favorably as shown in figure 6. The dissociation energy $D_0^{\circ}(\text{Y-C}_2)$ of 634 ± 19 kilojoules per mole (152 ± 5 kcal mole⁻¹) compares well with the value of 653 ± 21 kilojoules per mole (156 ± 5 kcal mole⁻¹) determined in reference 1. Likewise the heat of formation of $\text{YC}_2(\text{s})$, -91 ± 17 kilojoules per mole (-22 ± 4 kcal mole⁻¹) compares well with the previously reported value of -113 ± 25 kilojoules per mole (-27 ± 6 kcal mole⁻¹) obtained by De Maria et al. (ref. 1) who used a value of 410 kilojoules per mole (98 kcal mole⁻¹) for $\Delta H_{298, \text{vap}}^{\circ}$ for yttrium. If the value of 424.7 kilojoules per

mole ($101.5 \text{ kcal mole}^{-1}$) (ref. 13) is used for $\Delta H_{298, \text{vap}}^{\circ}$, then the data of De Maria et al. may be recalculated to give a value of -98 ± 21 kilojoules per mole ($-23.5 \pm 5 \text{ kcal mole}^{-1}$) which is in even better agreement with the present study.

Since the mass spectrometric method has been the only one employed for the determination of $\Delta H_{298, \text{f}}^{\circ}$ of $\text{YC}_2(\text{s})$ up to the present time, there is no other value available for comparison. However, the excellent agreement between second- and third-law enthalpies for reactions using $\text{YC}_2(\text{s})$, and the fact that $\text{YC}_2(\text{s})$ was positively identified as the solid Y-C phase present in our experiments, indicates that our value of $\Delta H_{298, \text{f}}^{\circ}$ is reliable.

The atomization energy of 2461 kilojoules per mole ($589 \text{ kcal mole}^{-1}$) for $\text{YC}_4(\text{g})$ suggests that this molecule is reasonably stable. In fact its stability is comparable to HoC_4 (ref. 4) and NdC_4 (ref. 3). Also, the verified existence of YC_4 suggests that the corresponding tetracarbides of scandium and lanthanum are stable molecules.

It is interesting to note that the Y- C_2 bond energy for the dicarbide and tetracarbide are almost equal. The comparison of the M- C_2 and M-O bond strengths that has been made for a number of metal oxide and dicarbide molecules (ref. 18) cannot be extended to the YC_4 case because the isoelectronic YO_2 molecule has not been observed. However, on the basis of the stability of YC_4 one may predict the existence of YO_2 as a stable molecule. Following the estimation procedure of Balducci et al. (ref. 3) we estimate a dissociation energy of 1464 kilojoules per mole ($350 \text{ kcal mole}^{-1}$) for YO_2 .

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 19, 1969,
129-03.

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